

935,981



## PATENT SPECIFICATION

NO DRAWINGS

935,981

Date of Application and filing Complete Specification: Dec. 19, 1961.

No. 45535/61.

Application made in Germany (No. F32859 IVa/45) on Dec. 28, 1960.

Complete Specification Published: Sept. 4, 1963.

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Index at acceptance:—Classes 2(3), C2C(1:5:7F); and 81(1), E1C(3B1:5D).

International Classification:—C07c. (A01n).

## COMPLETE SPECIFICATION

## Fungicidal Carbamic Acid Salts

We, FARBENFABRIKEN BAYER AKTIEN-  
GESELLSCHAFT, a body corporate organised  
under the laws of Germany, of 22c Lever-  
kusen-Bayerwerk, Germany, do hereby de-  
clare the invention, for which we pray that a  
5 patent may be granted to us, and the method  
by which it is to be performed, to be par-  
ticularly described in and by the following  
statement:—

10 The present invention is concerned with  
new fungicidal carbamic acid salts and with  
fungicidal compositions containing them.

From US Patent Specification No.  
2,317,765 alkylene-bis-dithiocarbamic acid  
15 salts are known which are distinguished by a  
good fungicidal activity. In this Specification  
there is described, *inter alia*, the preparation  
of an active compound of the aforesaid type  
by starting from propylene diamine, sodium  
20 hydroxide solution and carbon disulphide.

In a paper by Raymond W. Barratt and  
James G. Horsfall, Connecticut Agricultural  
Experiment Station, New Haven, Bulletin  
508, June 1947 entitled "Fungicidal Action  
25 of Metallic Alky Bisdithiocarbamates", there  
is further described (page 7) the disodium  
salt of isopropylene-bis-dithiocarbamic acid,  
and the Table on page 9 of this paper shows  
30 that the activity of the sodium salt of ethyl-  
ene-bis-dithiocarbamic acid is a multiple of  
that of the sodium salt of iso-propylene-bis-  
dithiocarbamic acid.

We have now found that the manganese salt  
35 of iso-propylene-bis-dithiocarbamic acid  
is distinguished by an especially good activity,  
particularly in comparison with the com-  
pounds described in the above-mentioned US  
Patent Specification. The activity of this iso-  
40 propylene compound is greater by a multiple  
than that of all the normal propylene com-  
pounds mentioned in the patent specification.

The finding that the manganese salt of iso-  
45 propylene-bis-dithiocarbamic acid possesses  
these extraordinary properties is especially  
surprising, since it is known from the above-

mentioned paper by Barratt and Horsfall that  
sodium salts show the contrary.

The compound according to the present in-  
vention can be prepared, for example, by  
reacting 1,2-propylene-diamine with carbon  
disulphide, preferably in the presence of an  
alkali metal hydroxide or ammonium hydrox-  
ide, and further reaction with salts of  
manganese.

The compound according to the present in-  
vention is active chiefly against fungal pests  
against which conventional dithiocarbamic  
acid salts have previously been employed, i.e.  
especially against *Phytophthora infestans*,  
*Cladosporium fulvum* or *Alternaria solani* on  
tomato and potato plants, against *Peronospora*  
(=*Plasmopara viticola*) on grape vines, *Ven-  
turia inaequalis* on fruits with pips, and  
against similar fungal pathogens of other  
plants.

The compound according to the present in-  
vention is applied in known manner, i.e. pre-  
ferably in combination with suitable solid or  
liquid extenders or diluents, optionally in the  
presence of suitable emulsifiers or wetting  
agents. The compound is preferably used in  
aqueous dilution, together with non-ionic  
emulsifiers and/or wetting agents, and, if de-  
sired, an inert solid formulation assistant. It  
may also be used with other fungicides and/or  
insecticides.

The production of the compound according  
to the invention may be briefly described as  
follows:—

0.255 kg. 1,2-propylene-diamine are dis-  
solved in 1.87 litres water. To this solution  
there are added dropwise 0.55 kg. carbon di-  
sulphide. 0.555 kg. of a 46% sodium hydrox-  
ide solution are then added.

The solution (0.833 kg. 100%) is further  
reacted with a manganese salt solution (man-  
ganese sulphate). Yield 0.426 kg. methyl-  
ethylene-bis(dithiocarbamic acid) manganese  
salt with 51.7% content (after splitting off  
carbon disulphide).

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[Price]

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According to a preferred method of production, the compound according to the present invention may also be produced directly from propylene dichloride, as can be seen from the following brief instruction.

5 37.7 g. propylene dichloride and 396.0 g. of a 35.8% ammonium hydroxide solution are reacted at 78—80° C. for 32 hours in an autoclave provided with stirrer, until the 10 propylene chloride disappears. The solution is concentrated to dryness *in vacuo* and the residue taken up in 210 ml. water.

To this aqueous solution there are added 15 80 g. of a 46% sodium hydroxide solution and 54 g. carbon disulphide at 38—40° C. (while maintaining a pH value of below 10) within about 8 hours. After the addition of a little kieselguhr, the solution is filtered off with suction. This solution is treated with an 20 aqueous solution of manganese sulphate and the precipitated manganese salt filtered off with suction and dried. Yield: 48 g. of 85% (after splitting off carbon disulphide) of methyl - ethylene - bis - (dithiocarbamic acid) 25 manganese salt.

Instead of the pure propylene chloride, a propylene chloride-containing petro-chemical by-product may be employed.

The following Example is given for the 30 purpose of illustrating the properties of the compound according to the present invention:—

#### EXAMPLE

Young tomato plants (Bonny Best) are sprayed drip-wet with aqueous suspensions 35 containing the active material in the concentrations given below. After 24 hours, the tomato plants are inoculated with a spore suspension of *Phytophthora infestans*. The plants are then placed in a humidity chamber with 100% atmospheric humidity and at a 40 temperature of 20° C. After a period of 5 days, the degree of attack is determined as a percentage based on the untreated but inoculated control plants. The degree of attack on the untreated control plants is taken as 100. The results obtained are given in the following Table:

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TABLE  
*Phytophthora infestans* on tomatoes

Active material	Concentration of active material in aqueous suspension in %	Degree of attack in % of the untreated control (=100): average value from 5 tests
1 Manganese-isopropylene-bis-dithiocarbamate (according to the invention)	0.025	5
zinc-isopropylene-bis-dithiocarbamate	0.025	12
2 manganese-isopropylene-bis-dithiocarbamate (according to the invention)	0.0062	16
manganese-ethylene-bis-dithiocarbamate	0.0062	21

- 50 As can be seen from the above Table, the fungicidal action of manganese-isopropylene-bis-dithiocarbamate is superior not only to that of zinc - isopropylene - bis - dithiocarbamate but also to that of manganese-ethylene-bis-dithiocarbamate: the plants treated with the fungicide according to the present invention show the smallest degree of attack by *Phytophthora infestans*.  
55 WHAT WE CLAIM IS:—  
60 1. The manganese salt of isopropylene-bis-dithiocarbamic acid.

2. Fungicidal compositions containing the manganese salt of isopropylene-bis-dithiocarbamic acid and a solid or liquid extender or diluent.

3. Fungicidal compositions according to claim 2, wherein there is additionally present an emulsifier and/or wetting agent.

4. Fungicidal compositions according to claim 2 or 3, wherein the liquid extender or diluent is water, together with a non-ionic emulsifier and/or wetting agent.

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5. Fungicidal compositions according to claim 2, substantially as hereinbefore described and exemplified.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1963. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.